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ITS CHARACTERISTICS AND APPLICATIONS

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NONMAGNETIC TIME-OF-FLIGHT MASS SPECTROMETER
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Hiroshi Tomita*

ABSTRACT

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In the nonmagnetic time-of-flight spectrometer (TOF), the gas or vapor to be analyzed is introduced into an ion chamber, and is ionized by electron bombardment.

The device allows high-rate, continuous analysis of mass spectra. The simplicity and versatility of the TOF are discussed. Operation of the Wiley type multiplier, recording, range, resolution, sensitivity, and accuracy of data are treated. Problem areas and the following applications are described: analysis of gas emanating from a gas chromatograph, tracing of a high-speed chemical reaction, ion decomposition and charge exchange study, ionic molecular reactions, high-temperature reaction thermodynamics, analysis of solids, analysis of gas in motion, chemical reactions, human breathing investigations and others. *Author*

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1. Introduction

The nonmagnetic time-of-flight mass spectrometer - abbreviated as /63* the TOF type - is an epoch-making mass spectrometer. Very rapid analysis of results has become possible. Many applications for various scientific fields have been developed. At present, this type is in practical use, mainly in the United States (Ref. 1). In 1962, it is estimated that one-third of the mass spectrometers being used in the United States are the TOF type.

Therefore, there are several research reports on the TOF type spectrometer, and its availability and problems are becoming apparent. Reports are also being made on the development of the equipment itself and the measurement techniques involved with the TOF spectrometer.

The TOF type has potentialities for a process-control analyzer, because of small size, light weight, and simple operation. We shall discuss its characteristics, problems, and applications for the benefit of possible users in this article.

2. Basic Principles

The principles of the TOF mass spectrometer have been given by Wiley (Ref. 2), Harrington (Ref. 3), and in several Japanese papers (Ref. 4, 5, 6) in detail. Therefore, the author will survey these very briefly.

Just as in the regular type of mass spectrometer, the gas or vapor to be analyzed - which is introduced into an ion chamber - is ionized by

* Note: Numbers in the margin indicate pagination in the original foreign text.

electron bombardment in the case of the TOF meter. The electron current is limited to the very short period of time in which the ionization takes place. A negative pulse is applied to an ion puller (see Figure 1), which withdraws the ions produced and sends them into the next accelerating region. A high electric field is produced by a high d.c. voltage applied to an ion accelerator. The ions increase their velocity due to the field, and pass into an ion separator.

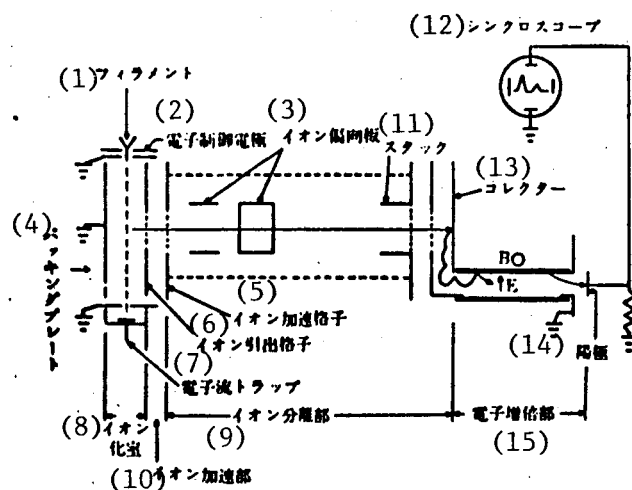


Figure 1

Schematic Diagram of the TOF Mass

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- (1)-Filament; (2)-Control Electrode for Electrons; (3)-Ion Deflection Plates; (4)-Backing Plate; (5)-Ion Accelerator; (6)-Ion Puller; (7)-Electron Trap; (8)-Ionization Chamber; (9)-Ion Separator; (10)-Region for Ion Acceleration; (11)-Stack; (12)-Syncroscope; (13)-Collector; (14)-Anode; (15)-Electron Multiplier

The ion separator is surrounded by a cylindrical metal mesh, which is maintained at the same potential as the accelerator, but there is no electric or magnetic field. The ions which pass through the accelerator fly along a straight path at a constant velocity and reach the collector. At the accelerator, each ion is given an energy which is

proportional to its electric charge (e), but is independent of its mass (m). Therefore, the velocity of the ions is proportional to $\sqrt{e/m}$, and the time of flight in the separator is proportional to $\sqrt{m/e}$ of each ion. If the generated ions have different m/e , they all pass through the accelerator in a very short time and enter the separator at almost the same time, but they are separated depending on each m/e in the separator. The ions which have the same value of m/e collect and form a group, and each group reaches the collector in turn, depending on their velocities. The m/e value is obtained by measuring the time of flight, and the amount of the ions is found by measuring the current at the collector.

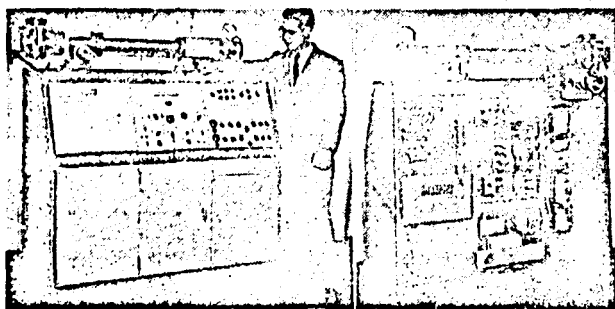


Figure 2

TOF Mass Spectrometer Made by Hokushin Electric Co.

This analytical operation is repeated at a high rate, and continuous results can be obtained. The output waveform is observed with a cyncroscope. A TOF mass spectrometer made by Hokushin Electric Company is shown in Figure 2. Figure 3 is an example of the mass spectrum (for *n*-butane) obtained from the cyncroscope.

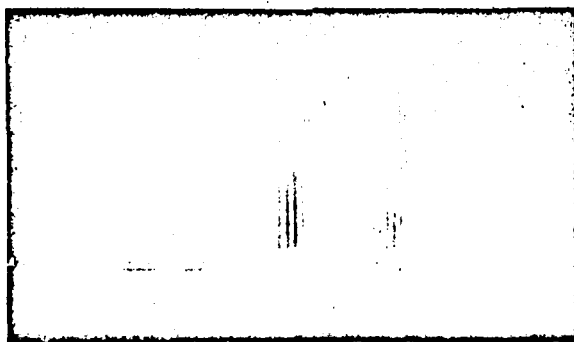


Figure 3
Mass Spectrum (n-butane)

3. Characteristics

3.1 High Speed Continuous Analysis

The TOF meter is suitable for high-speed analysis. In the other types of mass spectrometers, the voltage, current, or frequency must be scanned in order to measure the mass spectrum. In the TOF meter, however, nothing need be changed, because the TOF type includes a scanning operation in its basic principle. Therefore, the analyzing time of the TOF meter is the same as the period required for high-speed ions to pass through the separator, which is about 1 m long. Under standard conditions, it takes 100 μ s to measure 1 amu \sim 500 amu. This measurement can be repeated continuously. The analysis can be conducted in a shorter time, if the mass range to be measured is decreased. For an univalent ion, the relation between the mass (m amu) and the flight time (T μ s; 1 μ s = 10^{-6} sec) is:

$$T \propto \sqrt{2m}$$

3.2 Simplicity of Structure and Operation

The TOF meter has a simple structure, and is easy to operate. The

details are as follows:

(i) No electric and magnetic field is needed for the separator. In a magnetic-deflection type, a large electric magnet, which occupies a large percentage of the entire volume and weight, is necessary. A fine adjustment for locating the magnet is also a problem. The TOF meter, on the other hand, can be manufactured in a small size with less trouble, due to the adjustment. Furthermore, all the equipment can be placed on a carrier in order to take measurements at different locations.

(ii) The ion flight trajectory is a straight line, and the mechanical structure of the analyzer is rather simple. The ion source and the electron multiplier are installed at both ends of a large, straight analyzing pipe. This design makes the inside of the analyzer free of contamination, and also easy to clean. Removal of the electrodes is a simple process.

(iii) It was already mentioned that the TOF meter needs no scanning system. This again implies that no operation and adjustment in connection with the scanning system are necessary. The construction and handling become simple, for this reason.

(iv) No slit structure, which must be adjusted precisely, is used in an ion-lens system. Grid structures are used for that purpose. The ion source, in particular, is rather simple, and need not be extremely accurate. Therefore, the characteristic change due to electrode contamination does not represent a problem. The overhaul, cleaning, and reassembly of the ion source after operation over long

periods, or at the time of filament change, are quite easy.

3.3 Versatility of the Meter

As explained above, the structure of the ion source is rather simple, and the source is surrounded by empty space, in which extra devices can be installed. This is one of the merits of the TOF type. When the special studies are conducted - such as, measurements of high-speed reaction, the measurement of an ion-molecule reaction, and the analysis of solids using a high temperature furnace - it is often necessary to know the change in the ion source structure, or it is necessary to install other equipment close to the ion source. The ion source of the TOF meter can be changed rather easily, for the reason described above.

3.4 Wiley Type Electron Multiplier

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The Wiley type electron multiplier, by which secondary electrons from the collector are amplified, was developed by Wiley in the course of development of the TOF mass spectrometer.

The construction is simple and rigid, as compared to the old type. The characteristics are not changed when exposed to the atmosphere, and no aging treatment is necessary. The characteristics - such as, amplifier gain, frequency response, and noise figure - are all good enough to permit its use as an output amplifier of the TOF meter. Secondary electrons are generated at a conductive film, which is coated on a glass plate. The gain and stability of the amplifier change after being used a long time, due to a carbon compound which is deposited on the film surface. However, this part can be removed and washed; in this way, the

original characteristics are restored.

3.5 Output Recording

In order to take advantage of the high analysis speed, a high-speed camera is used to take pictures of the mass spectrum on the oscilloscope screen. On the other hand, an accurate recording can be carried out by a strip chart recorder, using an analog output system. This output system can operate any kind of recorder, under the condition that the output signal does not change during the time needed for the measurement. For instance, an automatic, balancing-type recorder, a pen oscillograph, and an electromagnetic oscillograph (using a light beam) can all be used. The analog output system and a memory scope are combined to record the mass spectrum (in single sweep image) in a shorter period.

The analog output system can be used to record a single peak continuously in the spectrum. Any type of recorder can be used for this purpose. A continuous recording of the single peak for each analyzing cycle can be taken by using intensity modulation with a cyncroscope. This method is convenient for the reaction measurement, in which the content of the sample in the ion source changes from time to time. The number of mass peaks which can be measured at the same time is two for a standard type, but it can be increased to six peaks by changing the electron multiplier and the analog output system.

3.6 Analysis Range and Resolution

The TOF meter analyzes from 1 amu to 5000 amu in one range, without range switching. The upper limit can be extended further, if

the repeating time for the analysis cycle is reduced.

The resolution is an important factor in the mass spectrometer. Wiley and co-workers concentrated on developing the resolution. With practical values of 1 m for the flight distance, and 3 kV for the accelerating voltage, a unit resolution of 200 amu is obtained. (The resolution has several definitions and is influenced by the technique employed. A definition used here is a limiting point, at which two mass peaks - with 1 amu difference between them - are clearly separated. There is an agreement between a theoretical value and an experimental one using a mercury isotope). A larger value of 350 amu, using a longer flight distance and a higher acceleration voltage, has been reported. This resolution value is enough for regular analysis, but not for special purposes - for example, the separation of N_2 , CO and C_2H_4 , for which a higher resolution is required. A double-constriction, magnetic deflection type must be used for that purpose.

In the TOF type, if the unit resolution is 200 amu, two peaks 2 amu apart from each other, at 400 amu, and those 8 amu apart, at 600 amu, can be separated. Thus, a constant separation is maintained up to the larger mass. This suggests that large-molecule analysis may be carried out, except for the case of isotope separation in which peaks are close together.

The resolution is changed by varying the speed of the analysis in the magnetic deflection type, but not in the TOF type. This is one reason why the TOF is suitable for high-speed analysis.

3.7 Absolute and Detection Sensitivity

Since it is usually assumed that the absolute sensitivity is (div/ μ Hg), including a sample introducer and the output recorder, no good reference data are available for the analyzer only. Since the TOF type has both advantages and disadvantages, in general the absolute sensitivity is almost the same as that of the magnet deflection type. The disadvantages are:

- (i) The generation time of the ion pulse is short;
- (ii) The pressure difference between the ion source and the ion separator is small because of the structure of the ion source.

The advantages are:

- (i) All the ions which are generated can be measured;
- (ii) The cross-sectional area of the ion flow is large because of no slit structure in the ion lens system;
- (iii) The output is amplified by the Wiley electron multiplier.

In a standard TOF meter with argon as a sample, the ratio of the sample pressure to the output current of a peak for Ar^{40} is about $30 \text{ mA}/10^{-6} \text{ Torr}$. The sample pressure was measured by a hot-cathode ion gauge, and the output current was the output of the electron multiplier.

In order to improve the disadvantages, we are considering:

- (i) An analyzing technique with a continuous ionization operation;
- (ii) Installing a separator with a hole between the ion source and the ion separator to increase the ion source pressure.

With respect to the sample amount needed for the analysis, the TOF type has an advantage, because the measuring time, as well as the absolute sensitivity, favor small amounts. For this reason, some new ideas are required for a sample-introduction device. For example, using a hot-filament type evaporation, the sample is placed very near to the electron flow, by which the sample is ionized. Very small amounts of the sample can be analyzed by this technique.

The detection sensitivity is calculated theoretically from the absolute sensitivity, the maximum sample pressure which is allowed in the ion source, and noise output.

A theoretical calculation, and an experiment for helium in air, show that an element content of more than 5 ppm is detectable.

3.8 Accuracy of Analysis

Relative analysis accuracy is determined by the stability of the meter. According to the experiments, the main factors affecting the stability of the TOF meter are: power voltage variation, fluctuation of the sample pressure in the ion source, and the amplification change in the electron multiplier. When all conditions are kept stable, a variation pattern, measured over several days, changes only 1% in standard deviation.

The TOF output is sensitive to statistical fluctuation. These fluctuations naturally take place in the course of transporting the ions to the collector, generating the ions, and during electron multiplication.

For the case of a small ion number in one cycle, such as less than

10^2 , the output variation is theoretically large. For measurements taking a long time, in which the strip chart recorder is used, the outputs are values which are averaged over each cycle, and this causes no problem. Therefore, when the output in each cycle is measured, a large amount of ions must be analyzed to avoid this statistical effect.

4. Problems

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4.1 Electron Tube Curcuits

A mechanical slit is used in the magnet-deflection type spectrometer. Electrical pulses which play the same role as mechanical slits, are adopted in the TOF meter. Therefore, the stability of the pulse heights, width, waveform, and also the stability of the d.c. source voltage, are important factors. The characteristics of a highly-sensitive d.c. amplifier and pulse generation circuits, which are both included in the analog output system, are also important. Generally speaking, the characteristics of the TOF meter depend greatly upon the electron tube circuits.

4.2 Vacuum System

The structure of the vacuum system is rather simple. However, it is necessary to use a pump having high pumping speed, because the analyzing pipe has a large volume in the TOF type, as compared to other types. The stability of the entire equipment is influenced by the stability of the pump. In the regular type of analysis, a separator can be placed between the ion source and the ion separator, in order to make the conductance small between them. This separator can decrease the effect of

the vacuum fluctuations in the ion separator. However, for the case of high speed analysis, in which a high pumping speed is required at the ion source, the pumping stability should be good because the separator cannot be used.

4.3 Electron Multiplier

When the dynode strips - which are a main element in the electron multiplier - are contaminated, the multiplication factor and the stability of the multiplier are changed. This matter should not be neglected during measurements, even though the dynode strips can be washed to recover their characteristics. The degree of contamination depends on the working conditions, but they should be washed once every one or two months. The following precautions for avoiding contamination are recommended:

(i) The pressure inside the analyzing pipe should be kept low. Placing a valve between the pipe and the evacuation system is effective.

(ii) The multiplication factor of the multiplier should be set as small as possible.

(iii) The contamination is mostly a carbonaceous deposit. A carbon compound should not be used too much - for example, in order to examine the sensitivity.

5. Applications

General applications of the TOF type take advantage of its ability to carry out high speed analysis. Namely, fast reactions, such as photo-chemical reactions and high-temperature reactions occurring in a shock wave, were studied. In these studies, the structural simplicity

around the ion source was fully utilized.

In the field of normal analysis, the TOF is being used for continuous analysis and micro analysis by taking advantage of its high speed and simplicity of handling. Other applications of the TOF meter are as follows: several studies on the properties of gaseous ions - such as an ionization reaction by electron bombardment and a reaction of ionic molecules, an analysis and determination of large molecular structure, a study of thermal dynamics of metals and inorganic solids using high-temperature furnaces. Some of them have already been analyzed with the magnetic-type meter, and the TOF type has comparable results, which are superior in some respects. Some applications in which the TOF type is advantageous will be described in detail.

5.1 Analysis of Gas Emanating from a Gas Chromatograph

As is generally known, a gas chromatograph cannot detect unknown samples reliably. For this reason, an infra red spectrometer or the mass spectrometer can be used only for qualitative analysis to obtain additional information. However, the use of the analyzer involves many troublesome operations, such as taking out the gas samples from the gas chromatograph at every measurement peak, and delicate handling of very small samples without contaminations. Therefore, this technique is not considered to be a good solution.

Adoption of the TOF type for this purpose has been already reported by Golke (Ref. 7) (in 1959), Ebert (Ref. 8) (in 1961), and other researchers (Ref. 9). In the United States, some examples are being

reported at present.⁽¹⁾

Since the TOF type has a short measuring time and a small absorption effect on gas in the ion source, the gas emanating from the gas chromatograph is introduced directly and analyzed without time delay. Only a variable leak valve, used to introduce a small amount of the gas, and some connecting pipes are necessary to connect the gas output and the meter. The output mass spectrum is recorded by taking pictures on the oscillograph screen or by using an electromagnetic oscillograph.

By combining the TOF meter and the gas chromatograph, one can carry out difficult analysis, which has been regarded as being practically impossible because of time and expense. Very unstable samples and samples expelled in very short times, namely 1/10 seconds, also can be analyzed. With an advanced type of gas chromatograph, which is a capillary column, the TOF type is more useful.

5.2 Tracing a High Speed Chemical Reaction

The mechanisms of chemical reactions have been studied with the mass spectrometer. However, the mechanisms were studied by analyzing elements in the sample before and after the reaction. It was impossible to measure the change in contents during the reaction, except for a very slow reaction. The reason is that the analyzing speed is slower than

(1) According to a users list: Bendix Company, E. I. du Pont, Dow Chemical, Monsanto Chemical, Esso, Atlantic Refining, Calvert Distilling, Eastman Kodak, Union Carbide, General Foods, Pittsburgh Plate Glass, General Electric, General Motors, General Dynamics, and Boeing are examples of users. There are more than ten companies.

the reaction speed.

The tracing of high speed reactions by using the TOF meter was tried by Kistiakowsky and others in 1957. His first problem was flash photochemical reactions. He reported (Ref. 10) that this technique was promising for studying high speed reactions and reaction probability, with examples of CH_2CO (ketene) and NO_2 decomposition.

Kistiakowsky also reported (Ref. 11, 12) that the decomposition /67 of N_2O and the oxidation of C_2H_2 (acetylene) occurred in the presence of a shock wave at high temperatures ($1000 \sim 2700^\circ \text{K}$). His technique was used by others. Diesen measured the velocity constant for thermal decomposition of Cl_2 in the temperature range from 1700 to 3200°K , using the shock wave and the TOF meter in 1963. The result agreed (Ref. 13) with a value obtained from an spectrometric experiment. Diesen also measured the thermal decomposition of N_2H_4 (hydrazine) at $1200 \sim 2500^\circ \text{K}$, and determined (Ref. 14) the velocity constants for five elemental reactions such as N_2H_2 , NH_3 , N_2 , H_2 , and NH_2 , by tracing their peaks on the mass spectrum. After that, Friedman reported on the thermal decomposition of phenolformaldehyde in a photo flash in 1963.

Burning, explosion and catalytic reaction can also be applied to this type of measurement.

The problems arising from the practical use of the TOF meter in this field are the sample introduction and the output signal recording. The mechanism of the sample introduction depends on the object to be measured and the type of reaction, and small modifications should be

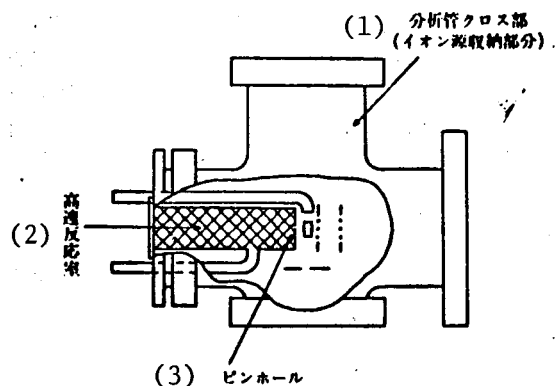


Figure 4

High-Speed Reaction Chamber (Ref. 3)

- (1)-End of the Analyzing Pipe (the Ion Source is Inside);
 (2)-High-Speed Reaction Chamber; (3) Pin Hole

carried out by each experimenter. Generally speaking, making the time delay for the sample introduction as short as possible, and avoiding additional reactions between the sample particle and the inside wall, are desirable. In many cases, the hot samples under high pressure are introduced into the ion source at room temperature under low pressure. For this purpose, the structure shown in Figure 4 is proposed. A cylindrical fast-reaction chamber is placed in contact with the backing plate, close to the ion source. The reaction takes place in the chamber, and the sample particles which are generated are introduced into the ionization chamber through a pin hole which is located at the center of the backing plate. A large pumping speed is required of the vacuum system, as compared to the case of the regular type of analysis. Sometimes, differential pumping, in which an extra vacuum system is attached to the ion source, is used. A high-speed camera

and intensity modulation (see 3 to 5) are used as methods of output signal recording.

5.3 Study of Ionization Phenomena

The mass spectrometer has been used for the study of ionization and dissociation of molecules. Since Fox introduced a retarding potential difference method (RPD method) by using single-energy electron flow, the accurate measurement of ionization efficiency curves, the measurement of ionization potentials and appearance potentials, and the study of ionization and dissociation have been carried out.

Kiser tried to use the TOF meter for this purpose in 1961. He employed Warren's extrapolated differential method and Lossing's semi-logarithmic method, rather than the RPD method. The appearance voltage was measured for the mass peak of C_2H_4O (ethylene oxide) and C_3H_6O (propylene oxide), and the expediency of the TOF type was shown (Ref. 16). Kiser also reported on experimental results obtained with sulphur compounds, such as C_2H_4S (ethylene sulphide), C_2H_5N (ethylenimine) (Ref. 17), C_3H_8S (2 - chia butane), $C_4H_{10}S$ (2 - chia pentane), and CH_3SSCH_3 (2, 3 - di-chia butane), and substituted oxiranes (Ref. 19), such as C_4H_6O (3, 4 - epoxy - 1 - butane), $C_4H_8O_2$ (1, - 2 - epoxy - 3 - metoxy propane), C_3H_5OCl (epichlorhydrin) and C_3H_5OBr (epibromhydrin).

A combination of the TOF meter and a pulsed RPD method was reported to be useful by Glick and Llewellyn in 1963, and by Melton and Hamill in 1963. Glick et al measured an IE curve precisely for N_2^+ and N^+ , and discussed the relation between excitation and detailed structures

around the ionization potential.

A calculation of the ionization cross section, taking Ar as a reference, was also carried out (Ref. 20). Melton et al made measurements with Kr^+ and C_2H_6^+ (fragment C_2H_5^+ , C_2H_4^+), and obtained good results (Ref. 21). The advantages of the TOF type in this field are:

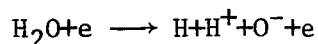
- (i) Modifying the apparatus for measurements is easy;
 - (a) Changing the electron gun is simple;
 - (b) Potential of the electron gun is close to ground potential, so that the floating RPD electrode is not necessary;
 - (c) Producing pulses for the pulsed RPD method is easy, because it has a pulse generator originally;
- (ii) Influence of initial ion energy on the measurement is avoided because a high voltage is used for the ion acceleration;
- (iii) The characteristics of the ion collection are good, because there is no slit in the ion lens system.

A fine grid electron gun is available for Fox's pulsed RPD method and for the method determining the critical energy with a space charge, as suggested by Cloutier and Schiff.

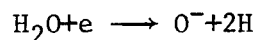
The generation mechanism of negative ions is different from that of positive ones. The IE curve must be made carefully, and no very successful results have been reported. The negative ion will be an interesting subject in the future, due to the fact that the generation of H_2O^- and O^- causes a misoperation in a GM tube and a proportional counter. Melton measured an IE curve for O^- generated from H_2O with

the TOF meter in 1963, and observed peaks due to the different generation mechanisms listed below. He also discussed (Ref. 21) the critical potential and resonance potential.

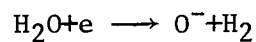
(i) Ion pair formation



(ii) Decomposition by capturing electrons



(iii) Rearrangement resonance capture



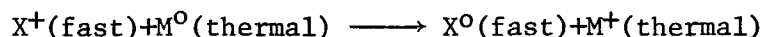
In the measurement of the ionization potential for negative ions /68 there is no reference value, as in the positive case obtained by a spectrometric method. Therefore, sometimes it is necessary to alternate between both ions frequently. The TOF type is again convenient for this purpose, because the switching between positive and negative ions can be readily done in the TOF.

The TOF has advantages for ionization other than electron bombardment, such as photoionization, ionization by radioactive rays, and ionization by electrical discharge. Fluegge reported on using the electrical discharge in 1961.

5.4 Ion Decomposition and Charge Exchange Study

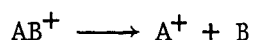
In the mass spectrometer, when accelerated ions from the ion source collide with other neutral molecules before reaching the collector, a charge transfer between them can occur. This phenomenon is prevented by reducing the pressure in the analyzing pipe. In the TOF type, this is likely to happen because of a long flight distance and of a low

pressure difference between the ion source and the analyzing tube. Since, in a simple charge transfer between ionic molecules a momentum transfer is very small, an ion which is newly generated by the collision stays at the same place, and a neutralized ion keeps flying with the same speed as before the collision.



Since the flight path is a straight line in the TOF type, the neutral particle will arrive at the collector with a very short delay as compared to other ions, and will generate secondary electrons which are measured as output. This increases deviations in the flight time, and lowers the resolution, which should be avoided. Therefore, by placing a cylindrical stack near the collector along the ion path, and by adjusting the potential applied to the electrode stack, the time required for the ions to arrive at the collector can be delayed and adjusted to that of the neutral particles (see Figure 1). When a reverse potential is applied to the electrode stack, the ions can be separated from the neutral particle. It is a well known technique by which the charge transfer cross-section between ions and molecules can be measured.

Hunt developed (Ref. 23) this idea further (1964) in order to measure the ion dissociation which can take place in the analyzing tube of the TOF meter. By placing a flat top potential barrier at some distance in the analyzing pipe, the original ions (AB^+) and fragment ion (A^+) generated by the dissociation and fragment neutral particle (B) can be separated from each other.



A^+ , B and AB^+ maintain almost the same speed, but when they pass the potential barrier, B is not affected by the potential and AB^+ is the second to arrive at the collector, due to large momentum, and A^+ is the third. They are separated in this way. The masses of A and B can be obtained by determining the time difference between AB^+ and B, and also between A^+ and B. Furthermore, the reaction rate may be obtained from the relationship between reaction time and the amount of the fragment ions, by changing the electrode location. The measurement results (Ref. 24) are not good enough yet, but future development is expected.

Another advantage of the TOF type - the fact that modification is readily performed - is being adopted. Wahrhaftig reported (Ref. 25) the measurement of ion dissociation using a home-made TOF mass spectrometer in 1959.

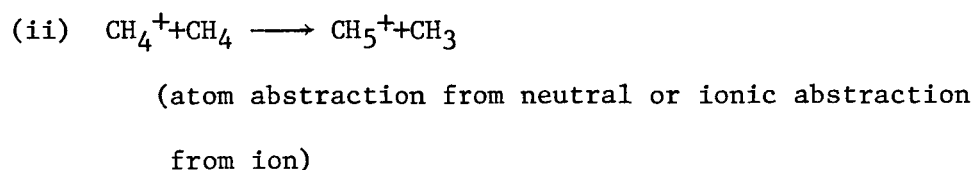
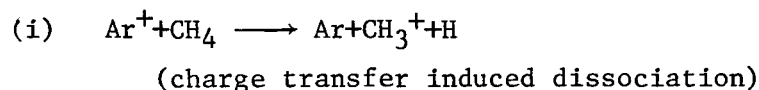
5.5 Ionic Molecular Reactions

It is a well-known phenomenon that a reaction takes place between ions and molecules in a gaseous reaction, such as discharge, burning and also in radioactive chemistry. The same reaction can occur in the mass spectrometer as reported in 1931.⁽²⁾ This reaction, however, has not been used positively for a long time. Since 1952,⁽³⁾ this has been utilized to determine the mechanism of the ionic molecular reaction.

(2) H. D. Smyth, Rev. Mod. Phys. 3, 347, 1931.

(3) V. L. Tal'roze, A. K. Lyubimova, Dokl. Akad. Nauk, SSSR 86, 909, 1952.

When the amount of the sample introduced into the meter is increased, and the pressure in the ion source is increased up to $10^{-5} \sim 10^{-4}$ torr, a great change in the mass spectrum is often observed because of the ionic molecular reaction. The size and relative location of the mass peaks suddenly change, and entirely new peaks can appear. Melton has used the magnetic deflection type, but recently - with the TOF type - measured (Ref. 21) the relation between the sample pressure and the change in the mass peak for the reactions:



This technique is simple, but restricted to some extent. A superimposition takes place with the fragment ions produced by electron bombardment, and with the ions produced by the essential reaction. The spectrum becomes complicated and difficult to analyze, because each fragment ion can take part in the reaction. The energy of the primary ions can not be changed so extensively, and the value of the energy cannot be measured correctly.

To solve this problem, Lindholm⁽⁴⁾ used two magnetic-type mass spectrometers. One causes a reaction between the primary ions, which

(4) E. Lindholm, Proc. Phys. Soc. London, A66, 1068, 1953.
E. Lindholm, et al., Arkiv. Fysik 18, 219, 1960

are introduced into the ion source of another, and the sample placed in the ion source. By this method, only desired ions can be taken out to produce reactions at a constant energy. Utilization of the TOF type for this purpose was already reported (Ref. 26) by Lehrle and Takahashi in 1961. They placed a Nier-type ion source close to the ion source of the TOF, and the ion flow generated here was introduced into the ionization chamber. Ar^+ , He^+ , N_2^+ , CO^+ were used as the primary ion, and hydrogen, benzene, toluene, and methane were used as the sample. The energy of the primary ion was increased up to 2000 eV. Furthermore, Lehrle modified the Nier-type ion source. By setting up a region in which the charge transfer takes place, neutral particle flow is introduced into the ion source of the TOF, and a reaction between the neutral particle and the samples can be observed (Ref. 27). They are planning to study the sputtering of solid samples and /69 neutral particles under excited conditions with this equipment.

In this area of reaction measurement, the TOF has the following advantages over the magnetic type:

(i) The electrical field in the ionization chamber is zero when the reaction takes place, because of pulse measurement;

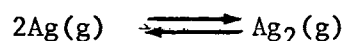
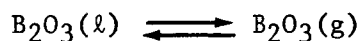
(ii) The structure of the ion source is simple, so that another ion source can be installed.

5.6 Thermodynamics of Reaction at High Temperature

The mass spectrometer can be applied to a measurement of thermodynamic characteristics, for low vapor pressure substances, such as solid salt, or more generally, for chemical reactions at high tempera-

ture. In this way, all of the gaseous elements flowing out of a high-temperature furnace, which is under phase equilibrium, can be analyzed qualitatively and quantitatively at the same time. In order to calculate the reaction heat, a slope method, which is based on the second law of thermodynamics, can be always used with a good approximation. These are the merits, as compared to methods employed up to the present, such as Knudsen or Langmuir's effusion method, and the transpiration method.

For this application, the magnetic type was first used, and was then replaced by the TOF type. White reported in 1961 that the TOF has advantages over the magnetic type. He rearranged the ion source of the TOF type. A Knudsen cell and a window, with which a photopyrometer is used to measure the temperature, were installed. Some basic reactions and the following reactions were measured (Ref. 28):



As for B_2O_3 , a relation between temperature and vapor pressure was obtained at $1220 \sim 1641^\circ \text{K}$, and the evaporation heat and the entropy of $\text{B}_2\text{O}_3(\text{g})$ closely agreed with values obtained by optical measurements. The IE curves were taken for B^+ , BO^+ , B_2O_2^+ as well as B_2O_3^+ , and it was concluded that the fragments were not produced in the Knudsen cell, but B_2O_3 was decomposed by electron bombardment. For Ag, the amount of Ag^+ was measured at $1235 \sim 1410^\circ \text{K}$, and the evaporation heat was calculated. For Ag_2 , the intensity ratio of Ag_2^+ to Ag^+ at four different

temperatures of 1380, 1413, 1460 and 1513° K, and the dissociation heat for Ag₂, which was obtained by this experiment, showed good agreement with the result obtained by the magnetic mass spectrometer.

White, et al made a series of experiments (Ref. 29, 30, 31, 32) for rare earth elements and their compounds with this equipment independently.

The characteristics of the TOF type meter for this application are as follows, with reference to White's report:

(i) The combination of the ion source and the high temperature Knudsen cell is easy. Accurate temperature measurement can be done by a photo pyrometer.

(ii) Flow direction of the gas from the Knudsen cell can be made perpendicular to the direction of the electron flow and the ion flow. Molecules under measurement and those in the background can be separated due to this fact. By setting an electric field between the Knudsen cell and the ion source, the ions produced in the cell can be measured.

(iii) It is difficult to control the temperature of the Knudsen cell at a high temperature. If it takes a longer time for the measurement, the result becomes less accurate. At a very high temperature, short measurement time is especially required, because of the lifetime of cell material. The TOF type is convenient for this, because of its short measuring time. If more than two analog output systems are used, different points in the spectrum can be measured at the same time, so that the recording time is reduced.

(iv) We observed 1 amu difference in the mass peak at 200 amu.

Therefore, the resolution limit is not a problem.

(v) With respect to sensitivity, a minimum measurable sample pressure is 10^{-8} Torr for White's meter. This is one decade larger, but is developed by adopting continuous ionization.

5.7 Analysis of Solids and Determination of Structure of Large Molecules

Solids having a considerable vapor pressure at about 200° C can be handled by a regular feeding system, but for most solids a special high-temperature device has to be used. The hot filament type and a Knudsen cell are used for this purpose.

In the hot-filament type, the sample is loaded on a boat made of W, Re or Ta, and the electric current flows through the boat to evaporate the sample at up to 1000° C. This has the following merits:

(i) The sample can be very near the electron flow, so that the evaporated sample is effectively analyzed.

(ii) Temperature can be controlled by a thermocouple type thermometer.

(iii) Samples are changed readily, by using an additional vacuum system.

Even for a sample handled at low temperature, the hot filament type is recommended in the case when the sample amount is small and the sample activity is strong.

A combination of the TOF meter and the hot filament can be used for micro analysis and the structure determination of large molecules. For example, very small amounts of the sample - as in the case of newly-discovered organics - can be analyzed by the TOF type. According to a

report by Bendix, cholesterol was analyzed at 50° C, and a main peak was observed at 380 amu. The hot filament can be used for research on isotope reactions as a surface ionization source. One example was reported by Studier et al (Ref. 33). They attached a single filament made of W and Re to the TOF meter, and UC_2^+ , U^+ , UO^+ , UO_2^+ , and UO_3^+ , produced from sample U, were measured.

The Knudsen cell is a method by which the sample is loaded in a crucible made of W or Ta, and heated by an electrical heater or electron bombardment. The evaporated sample is introduced into the ionization chamber through a slit. Usually, it is used at 1000 ~ 3000° K. (See Figure 5.)

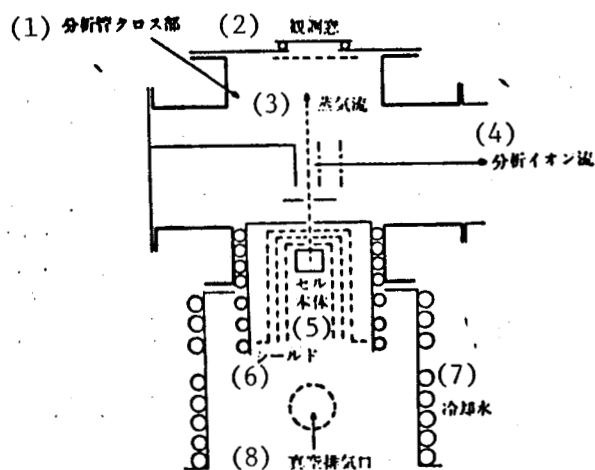


Figure 5

/70

Connection with Knudsen Cell

- (1)-Analyzing Pipe; (2)-Observation Window; (3)-Vapor Flow;
 (4)-Ion Flow; (5)-Cell; (6)-Shield; (7)-Cooling Water;
 (8)-Vacuum Pumping Pipe

A combination of the TOF and the Knudsen cell has already been described.

As methods of analyzing solids, a discharge method (Ref. 22) and a sputtering method (Ref. 27) are suitable applications of the TOF type as described above. The discharge method has the advantage that the sensitivity for every element is constant. Since ions produced by discharge have a wide energy distribution, a Herzog-Mattauch type mass spectrometer is usually necessary, but Fluegge used the TOF type for this application in 1961 (Ref. 22). He used a collimating slit for introducing the ions produced by the discharge, and obtained modest resolution by making the ion flow parallel to the pulling grid. An ion component parallel to the grid is readjusted by the deflection plates. By this technique, the ions within a rather narrow velocity region can be analyzed, after passing an energy filter which is made of the deflection plates. In principle, this looks as though two TOF meters are connected at right angles to each other. Fluegge measured Si^+ , Si^{2+} , Si^{3+} , Si^{4+} from a Si sample, and Cu^+ , Cu^{2+} and Cu^{3+} from a Cu electrode, and reported that the ratio of high-valency ions decreases by a factor of 1/5 as ionization increases. Also, the ratio of Cu isotopes is $^{63}\text{Cu} : ^{65}\text{Cu} \div 1 : 0.43$ (this ratio is 1:0.47 in the Physics Handbook). Neutral particles generated by discharge can also be measured by this meter.

5.8 Analysis of Gas in Motion

Gaseous samples having a velocity in a constant direction can be well analyzed by the TOF meter. The direction of gas flow can be set at right angles to electron and ion flow without decreasing the resolution. This is generally called a right-angle inlet system.

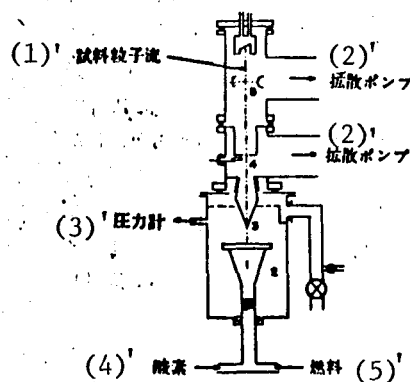


Figure 6

Connection with a Burner (Ref. 34)

(1)'-Sample Particle Flow; (2)'-Diffusion Pump; (3)'-Pressure Gauge; (4)'-Oxygen; (5)'-Fuel;

1: Burner; 2: Burning Chamber; 3: Quartz Probe; 4: Opening;
5: Ion Source of Mass Spectrometer

Applications of the Knudsen cell and the discharge have already been given, but they can also be applied to research on burning and plasma, and an analysis of the atmosphere using earth satellites.

Homann and Machizuki (Ref. 34) analyzed the gas inside a long flame by the TOF meter. Acetylene, ethylene, propane or benzene are mixed with oxygen, and are burned under a pressure of 20 ~ 60 mm Hg. Samples are taken out by a quartz probe, and introduced into the ion source through the right-angle system (see Figure 6). The same experiment can be performed by the magnetic type, but the TOF type is more advantageous because of the right-angle inlet system.

O'Halloran reported (Ref. 35) in 1963 that a two-stage supersonic nozzle was designed for taking samples out of a high-energy plasma

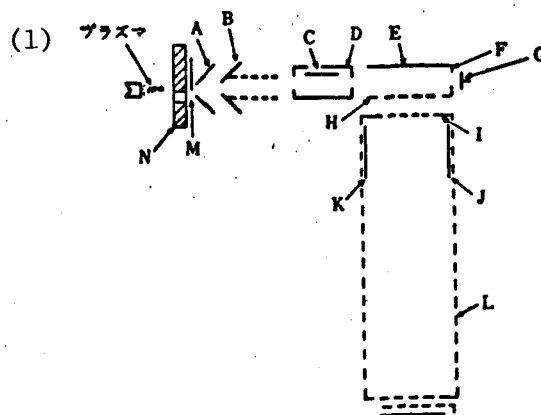


Figure 7

Connection with Plasma Generator (Ref. 35)

(1)-Plasma

A: First Orifice; B: Second Orifice; C: Deflection Plate;
 D: Deflection Shield; E: Packing; F: Shield for Ion Trap;
 G: Ion Trap; H: Ion Pulling Grid; I: Ion Accelerator;
 J, K: Deflection Plates; L: Separator; M: Sealing;
 N: Graphite Shutter

and for directly introducing them into the TOF ion source (see Figure 7).

The mass peaks for A, N_2 , O_2 , H_2O , A^+ , N_2^+ and H_2O^+ were measured in an argon plasma operating at atmospheric pressure. The relation between location and gas content in the plasma, and that between electrical power and gas concentration, were discussed. The results obtained showed that N^+ and O^+ are found in the plasma, but N and O are not found. The electrical power and output of A^+ and N_2^+ are correlated in a linear equation, and the ion density is $1 \times 10^{13} \sim 5.2 \times 10^{12}$ ions/cm³.

In order to analyze gases at high altitudes, a mass spectrometer is being placed on an earth satellite in the United States. In this

case, the meter is moving at very high speed with respect to the gases being tested. The TOF is again useful, because of the right angle inlet system.

The characteristics of the right angle system are as follows:

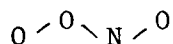
- (i) Moving gases can be analyzed.
- (ii) Velocity distribution of the sample can be measured. /71
- (iii) Ions, either in a continuous form or in a pulse, can be measured.
- (iv) There is no background effect in the ion measurement. For the measurement of neutral particles, by placing the electron current flow slightly out of the center of the ion flow, placing a certain time interval between ionization and the measurement, and using the deflection plate as an energy filter, the background effect can be avoided.

5.9 Other Applications

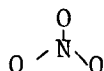
Several examples of the applications are as follows:

- (i) Study of chemical reactions, using isotopes. Clyne used the TOF mass spectrometer to study chemical reactions using isotopes in 1961 (Ref. 36). O^{16} and O^{18} were measured as products of the reaction, $O + NO_2 = NO + O_2 + 46 \text{ kcal/mol}$, and it was concluded that NO_3 did not produce an unbalanced configuration⁽⁵⁾, but rather a triangular form⁽⁶⁾ in the course of the reaction.

(5) Unbalanced configuration



(6) Triangular complex



(ii) A study of breathing. Lee analyzed air in a human lung by the TOF mass spectrometer (Ref. 37). The purpose was to examine sick individuals, using pilots of high-speed airplanes. A healthy man breathes oxygen for 5 ~ 10 minutes, then stops breathing for a short time. The decrease in the lung capacity and contents before and after cessation of breathing are measured. Results showed that there is no N_2 and CO_2 passing from the blood into the lung during the cessation, and the decrease in capacity is proportional to the time of breath cessation. It was reported that the capacity decrease is determined by oxygen consumption. O'Halloran described the TOF meter used in that experiemnt in 1961 (Ref. 38). The same experiments are being conducted in many places.⁽⁷⁾

(iii) Residual gas of high vacuum. The ion source of the TOF meter was inserted into a vacuum chamber, in order to measure the residual gas of the vacuum (Ref. 39).⁽⁸⁾ The change in content of the residual gas is checked without delay by this technique.

(iv) Process monitoring. The TOF meter has not been applied to process monitoring. The reason is that not enough experience has been accumulated with the TOF, because extremely high reliability is required for the process instruments. But the TOF meter has many advantages

(7) According to a users list of Bendix Co., Bellvue Hospital, Brooks Air Force Base, Boston University, General Dynamics, New York Hospital and Newark Presbyterian Hospital are using it for this purpose.

(8) According to the users list of Bendix Co., NASA, ARO, Boeing are using it for this experiment.

which are suitable for this application. This is a very promising field.

6. Conclusion

The main applications of the TOF type mass spectrometer have been introduced in this article. At present, the number of TOF meters being used is increasing rapidly. General reports on research using this mass spectrometer in various fields will be published within several years.

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